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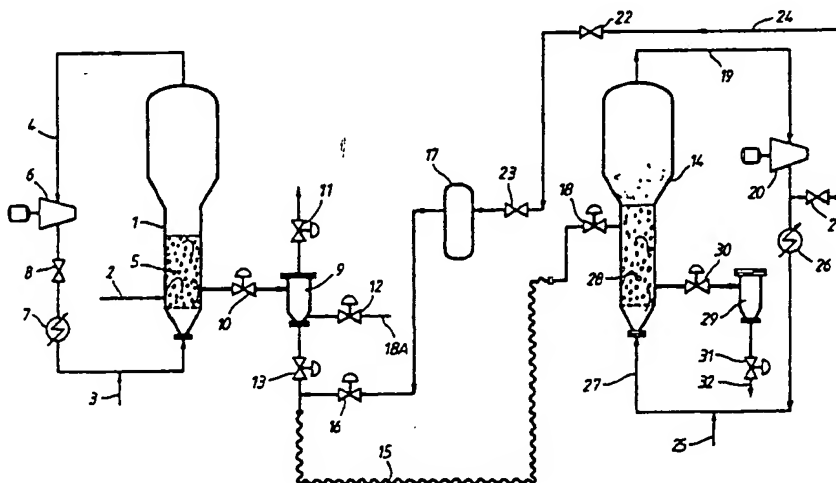
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(54) Improved ethylene polymer film resins.

(57) A class of relatively high molecular weight, high density ethylene polymers (HMW-HDPE) is disclosed capable of being formed into thin films of high strength, such polymers having a density of at least about 0.935 g/cc, a flow index (I_{21}) no higher than about 15 g/10 min., a melt flow ratio (MFR) of at least about 65, and a dynamic elasticity at 0.1 rad./sec. of no higher than about 0.7 at a corresponding complex viscosity at 0.1 rad./sec. no higher than about 14E5, i.e., about 14×10^5 poises.

Such polymers are produced by the use of two gas-phase reactors in series. In the first reactor a HMW polymer is produced having a density of at least 0.910 g/cc, while in the second reactor a LMW polymer is produced having a density of at least 0.940 g/cc.



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This invention relates to relatively high molecular weight, high density ethylene polymers capable of being formed with good processability into films having improved mechanical properties.

In accordance with this invention, relatively high molecular weight, high density ethylene polymers (HMW-HDPE) capable of being formed into thin films of high strength are provided, such polymers having a density of at least about 0.925 g/cc, a flow index (I_{21}) no higher than about 15 g/10 min., a melt flow ratio (MFR) of at least about 65, and a dynamic elasticity (as defined hereinafter) at 0.1 rad./sec. of no higher than about 0.70 at a corresponding complex viscosity at 0.1 rad./sec. no higher than about 14E5, i.e., about 14×10^5 poises.

The ethylene polymer of this invention will in most cases consist essentially of a bimodal blend of relatively high molecular weight (HMW) and low molecular weight (LMW) ethylene polymers with the HMW component present, for example, at a weight fraction of at least about 0.5 of such ethylene polymer content and having a density of at least about 0.910 g/cc, a flow index (I_{21}) of, for example, no higher than about 0.8g/10 min., a relatively narrow molecular weight distribution indicated by a flow ratio (FR), for example, no higher than about 15, and a dynamic elasticity at 0.1 rad./sec., for example, of no higher than about 0.75 at a corresponding complex viscosity at 0.1 rad./sec. of no higher than about 7E6, i.e., 7×10^6 poises, and the LMW component having a density of at least about 0.940 g/cc and a melt index (I_2) of at least about 100 g/10 min.

The HMW-HDPE product of this invention having relatively low elasticity and molecular weight distribution indicated by MFR, can be formed with good processability into thin gauge films having excellent mechanical properties, e.g., Dart Drop Impact and Elmendorf Tear resistance, despite the fact that its short chain branching, e.g., ethyl groups per 1000 C atoms, appears to be higher in the LMW component than in the HMW component. This is contrary to a prevailing belief that short chain branching should be concentrated in the HMW component for optimum mechanical properties of films.

The drawing is a schematic diagram of a gas phase tandem polymerization process which can be used to make the products of this invention.

The ethylene polymer of this invention preferably consists essentially of either 1) a homopolymer of ethylene; 2) at least one copolymer of a preponderance of ethylene with a minor amount of a 1-olefin containing 3 to 10 carbon atoms, e.g., 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof; or 3) a mixture of any of the foregoing polymers. In general, the polymer product will comprise an amount of polymerized comonomer which is, for example, from 0 to 30 weight percent, based on the total weight of polymer.

The density of the ethylene polymer product of this invention will generally be, for example, at least 0.925 g/cc, preferably 0.940 to 0.960 g/cc, and most preferably 0.943 to 0.952 g/cc.

The flow index or high load melt index of the ethylene polymer of this invention (I_{21} , measured at 190°C in accordance with ASTM D-1238, Condition F) is generally no higher than 15, preferably from 4 to 12, and most preferably 5 to 10 g/10 min., while the melt flow ratio (MFR), defined as the ratio of flow index (I_{21}) to melt index (I_2), measured at 190°C in accordance with ASTM D-1238, Condition E, is at least 65, preferably 75 to 180, and most preferably 80 to 150.

The dynamic elasticity of the polymer product of the invention is no higher than 0.7 at 0.1 rad./sec. at a corresponding complex viscosity of no higher than 14E5 (14×10^5 poises) at 0.1 rad./sec., preferably 0.45 to 0.65 at a corresponding complex viscosity of 6E5 to 14E5, and most preferably 0.45 to 0.60 at a corresponding complex viscosity of 7E5 to 14E5.

The dynamic elasticity as used herein is defined as the ratio of the storage modulus $G'(w)$ to the loss modulus $G''(w)$. The following definitions of these moduli were adapted from those given in J.D. Ferry, Viscoelastic Properties of Polymers, 3rd Edition (New York: John Wiley & Sons, 1980) 41-42. The definitions pertain to measurements made in small strain oscillatory measurements.

Storage Modulus, $G'(w)$ is defined as the stress in phase with the strain in a sinusoidal shear deformation divided by the strain. It is a measure of the energy stored and recovered per cycle, when different systems are compared at the same strain amplitude. It is a function of the oscillating frequency w .

Loss Modulus, $G''(w)$ is defined as the stress 90 degrees out of phase with the strain divided by the strain. It is a measure of the energy dissipated or lost per cycle of sinusoidal deformation, when different systems are compared at the same strain amplitude. It is also a function of the oscillating frequency w .

Complex Viscosity is derived from $G'(w)$ and $G''(w)$ as hereinbefore defined using the following equation:

$$\text{Complex Viscosity} = \frac{G'(w)}{w} + \frac{G''(w)}{w}$$

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As stated, the ethylene polymer of this invention will in cases consist essentially of a bimodal blend of relatively high molecular weight (HMW) and low molecular weight (LMW) ethylene polymers with the HMW component being present, for example, at a weight fraction of at least 0.5 of the ethylene polymer content. Such HMW component is preferably present at a weight fraction of 0.5 to 0.65, more preferably 0.51 to 0.60, with the remainder of the ethylene polymer being the LMW component. In addition, the HMW component will generally have a density of at least 0.910 g/cc, preferably 0.920 to 0.935 g/cc, and are preferably 0.924 to 0.935 g/cc; a flow index or high load melt index (I_{21}) of no higher than 0.8, preferably from 0.15 to 0.7, and more preferably 0.2 to 0.6 g/10 min.; a flow ratio (FR, defined as the ratio of flow index [I_{21}] to intermediate load melt index [I_5], measured at 190° C under a load of 5 kilograms in accordance with ASTM D-1238, Condition P) of no higher than 15, preferably 8 to 14, and more preferably 9 to 13; and a dynamic elasticity no higher than 0.75 at 0.1 rad./sec. at a corresponding complex viscosity of no higher than 7E6 (7×10^6 poises), at 0.1 rad./sec., preferably 0.45 to 0.7 at a corresponding flex viscosity of 2E6 to 6E6, and more preferably 0.5 to 0.65 at a corresponding complex viscosity of 3E6 to 6E6.

The LMW component will generally have a density of at least 0.940 g/cc, preferably 0.945 to 0.970 g/cc, and most preferably 0.950 to 0.970 g/cc, and a melt index (I_2) of at least 100 g/10 min., preferably 200 to 2000 g/10 min., and more preferably 300 to 1500 g/10 min.

The ethylene polymer product of this invention is capable of being formed into thin gauge films, e.g., of up to 1.5 mil., of superior mechanical properties, e.g., an Elmendorf tear resistance in the machine direction (MD Tear, ASTM D1922) of at least 10 g/mil, preferably 15 to 60 g/mil, and more preferably 20 to 60 g/mil, and a Dart Drop Impact resistance (F_{50} , ASTM D1709) of at least 200 g, preferably 200 to 600 g, and more preferably 250 to 600 g.

When the ethylene polymer of this invention consists essentially of HMW and LMW ethylene polymer components as previously described, such components may be prepared separately and physically blended in a conventional manner, e.g., by initially dry blending the resin in a mixer with suitable additives, and then melt blending it in an extruder. The relative proportions of the HMW and LMW components are such that the blending produces an ethylene polymer product having the desired properties of density, flow index (I_{21}), melt flow ratio (MFR), and dynamic elasticity as set out hereinbefore.

Preferably, however, the desired bimodal ethylene polymer blend is directly produced by means of a gas phase, fluidized bed, tandem reactor process. Whichever method is used, the described desirable properties of the ethylene polymer obtained are dependent on the catalyst used to polymerize both components and particularly the HMW component, as well as the process conditions.

In utilizing a gas phase, fluidized bed, tandem reactor process to obtain the product of this invention, bimodal ethylene polymer blends having the described combination of good processability and superior mechanical properties are produced by a process including the steps of polymerizing gaseous monomeric compositions comprising a major proportion of ethylene in at least two gas phase, fluidized bed reactors operating in the tandem mode under the following conditions. In the first reactor, a gas comprising monomeric composition and, optionally, a small amount of hydrogen, is contacted under polymerization conditions with an appropriate Ziegler-Natta or coordination catalyst as described more fully hereinafter, comprising a transition metal compound as primary catalyst component and a reducing agent such as an organometallic compound as cocatalyst, at a hydrogen/ethylene molar ratio of no higher than 0.3 and an ethylene partial pressure no higher than 100 psia such as to produce a relatively high molecular weight (HMW) polymer powder wherein the polymer is deposited on the catalyst particles. The HMW polymer powder containing the catalyst is then transferred to a second reactor with, optionally, additional cocatalyst which may be the same or different from the cocatalyst utilized in the first reactor but with no additional transition metal catalyst component, together with a gaseous mixture comprising hydrogen and monomeric composition wherein additional polymerization is carried out at a hydrogen/ethylene molar ratio of at least 0.9, the ration being sufficiently high such that it is at least 8.0 times that in the first reactor, and an ethylene partial pressure at least 1.2 times that in the first reactor, to produce a relatively low molecular weight (LMW) polymer much of which is deposited on and within the HMW polymer/catalyst particles from the first reactor, such that the fraction of HMW polymer in the bimodal polymer leaving the second reactor is at least 0.5.

The foregoing conditions provide for a process wherein the production of fines tending to foul compressors and other quipment is kept to a relatively low level. Moreover, such conditions provide for an

inhibited level of productivity in the first reactor with a resulting increased level of productivity in the second reactor to produce a bimodal polymer blend having properties as previously described and a high degree of homogeneity (indicated by low level of gels) caused by a substantial degree of blending of HMW and LMW polymer in each final polymer particle inherently resulting from the process operation. The bimodal blend is capable of being processed without undue difficulty into films having a superior combination of mechanical properties.

The gaseous monomer entering both reactors may consist wholly of ethylene or may comprise a preponderance of ethylene and a minor amount of a comonomer such as a 1-olefin containing 3 to 10 carbon atoms. Comonomeric 1-olefins which may be employed are, for example, 1-butene, 1-pentene, 1-hexane, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. The comonomer may be present in the monomeric compositions entering either or both reactors.

In many cases, the monomer composition will not be the same in both reactors. For example, the monomer entering the first reactor may contain a minor amount of comonomer such as 1-hexane so that the HMW component of the bimodal product is a copolymer, while the monomer fed to the second reactor may consist essentially of ethylene so that the LMW component of the product is substantially an ethylene homopolymer. The amount of comonomer may be, for example, from 0 to 30, preferably 0 to 20 weight percent, based on the total weight of polymer produced in the tandem process.

Hydrogen may or may not be used to modulate the molecular weight of the HMW polymer made in the first reactor. Thus, hydrogen may be fed to the first reactor such that the molar ratio of hydrogen to ethylene (H_2/C_2 ratio) is, for example, up to 0.3, preferably 0.005 to 0.2. In the second reactor it is necessary to produce a LMW polymer with a low enough molecular weight and in sufficient quantity so as to produce bimodal resin which can be formed, with a minimum of processing difficulties, into films having a superior combination of mechanical properties. For this purpose, hydrogen is fed to the second reactor with the ethylene containing monomer such that the hydrogen to ethylene mole ratio in the gas phase is at least 0.9, preferably 0.9 to 5.0 and most preferably from 1.0 to 3.5. Moreover, to provide a sufficient difference between the molecular weights of the polymers in the first and second reactor so as to obtain a bimodal resin product having a wide enough molecular weight distribution necessary for the desired levels of processability and mechanical properties, the hydrogen to ethylene mole ratios in the two reactors should be such that the ratio in the second reactor is at least 8.0 times the ratio in the first reactor, for example from 8.0 to 10,000 times such ratio, and preferably 10 to 200 times the ratio in the first reactor.

Utilizing the hydrogen to ethylene ratios set out previously to obtain the desired molecular weights of the HMW and LMW polymers produced in the first and second reactors respectively tends to result in relatively high polymer productivity in the first reactor and relatively low productivity in the second reactor. This tends to result in turn in a bimodal polymer product containing too little LMW polymer to maintain satisfactory processability. A significant part of this invention lies in the discovery that this effect can be largely overt by employing ethylene partial pressures in the two reactors so as to reduce the polymer productivity in the first reactor and raise such productivity in the second reactor. For this the ethylene partial pressure employed in the first reactor is no higher than 100 psia, for example from 15 to 100 psia, preferably from 20 to 80 psia and the ethylene partial pressure in the second reactor is, for example from 26 to 170 psia, preferably 55 to 120 psia, with the ethylene partial pressures in any specific process being such that the ratio of ethylene partial pressure in the second to that in the first reactor is at least 1.2, preferably 1.25 to 7.0, and more preferably 1.25 to 4.0.

If desired for any purpose, e.g., to control superficial gas velocity or to absorb heat of reaction, an inert gas such as nitrogen may also be present in one or both reactors in addition to the monomer and hydrogen. Thus the total pressure in both reactors may be, for example, from 100 to 600 psig, preferably 200 to 350 psig.

The temperature of polymerization in the first reactor may be, for example, from 60 to 130°C, preferably 60 to 90°C, while the temperature in the second reactor may be, for example, from 80 to 130°C, preferably 90 to 120°C. For the purpose of controlling molecular weight and productivity in both reactors, it is preferred that the temperature in the second reactor be at least 10°C higher, preferably 20 to 60°C higher than that in the first reactor.

The residence time of the catalyst in each reactor is controlled so that the productivity is suppressed in the first reactor and enhanced in the second reactor, consistent with the desired properties of the bimodal polymer product. Thus, the residence time may be, for example, 0.5 to 6 hours, preferably 1 to 3 hours in the first reactor, and, for example, 1 to 12 hours, preferably 2.5 to 5 hours in the second reactor, with the ratio of residence time in the second reactor to that in the first reactor being, for example, from 5 to 0.7, preferably 2 to 0.8.

The superficial gas velocity through both reactors is sufficiently high to disperse effectively the heat of reaction so as to prevent the temperature from rising to levels which could partially melt the polymer and shut the reactor down, and high enough to maintain the integrity of the fluidized beds. Such gas velocity may be, for example, from 40 to 120, preferably 50 to 90 cm/sec.

The productivity of the process in the first reactor in terms of grams of polymer per gram atom of transition metal in the catalyst multiplied by 10^6 , may be in the range, for example, of 1.6 to 16.0, preferably 3.2 to 9.6; in the second reactor, the productivity may be, for example, from 0.6 to 9.6, preferably 1.6 to 3.5, and in the overall process, the productivity is, for example, from 2.2 to 25.6, preferably 4.8 to 16.0. The foregoing ranges are based on analysis of residual catalyst metals in the resin product.

If it is desired to prepare the HMW and LMW components separately and subsequently physically blend them, each component may be produced in a single stage gas phase fluidized bed reactor employing process conditions within the ranges described for the two reactors utilized in the foregoing gas phase tandem reactor process. In either case, the specific process conditions are chosen in combination with an appropriate catalyst and weight fractions of the two components so as to obtain a final bimodal polymer having the desired combination of properties.

One suitable class of Ziegler-Natta catalysts for the preparation of the polymer products of this invention comprises:

- (i) a catalyst precursor complex or mixture of complexes consisting essentially of magnesium, titanium, a halogen, and an electron donor as hereinafter defined supported on an inorganic porous carrier; and
- (ii) at least one hydrocarbyl aluminum cocatalyst.

The titanium based complex or mixture of complexes is exemplified by an empirical formula $Mg_aTi(OR)_bX_c(ED)_d$ wherein R is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR group is alike or different; X is Cl, Br, or I, or mixtures thereof; ED is an electron donor, which is a liquid Lewis base in which the precursors of the titanium based complex are soluble; a is 0.5 to 56; b is 0, 1, or 2; c is 1 to 116, particularly 2 to 116; and d is 2 to 85. The complex is formed by reacting appropriate titanium and magnesium compounds in the presence of an electron donor.

A titanium compound which can be used to prepare the foregoing complex has the formula $Ti(OR)_aX_b$ wherein R and X are as defined for component (i) above; a is 0, 1 or 2; b is 1 to 4; and a + b is 3 or 4. Suitable compounds are $TiCl_3$, $TiCl_4$, $Ti(OC_6H_5)_3$, $Ti(OCOCH_3)_3$ and $Ti(OCOC_6H_5)_3$.

A magnesium compound which may be reacted with the foregoing titanium compound to form the complex has the formula MgX_2 wherein MgX_2 X is as defined for component (i) above. Suitable examples are $MgCl_2$, $MgBr_2$, and MgI_2 . Anhydrous $MgCl_2$ is a preferred compound. About 0.5 to 56, and preferably about 1 to 10, moles of the magnesium compound are used per mole of titanium compound.

The electron donor present in the catalyst composition is an organic compound, liquid at temperatures in the range of about 0°C to about 200°C. It is also known as a Lewis base. The titanium and magnesium compounds are both soluble in the electron donor.

Electron donors can be selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ketones, aliphatic amines, aliphatic alcohols, alkyl and cycloalkyl ethers, and mixtures thereof, each electron donor having 2 to 20 carbon atoms. Among these electron donors, the preferred are alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; dialkyl, diaryl, and alkaryl ketones having 3 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms. The most preferred electron donor is tetrahydrofuran. Other examples of suitable electron donors are methyl formate, ethyl acetate, butyl acetate, ethyl ether, dioxane, di-n-propyl ether, dibutyl ether, ethyl formate, methyl acetate, ethyl anisate, ethylene carbonate, tetrahydropyran, and ethyl propionate.

The cocatalyst may, for example, have the formula $AlR''_eX'R_fH_g$ wherein X' is Cl or OR''; R'' and R' are saturated aliphatic hydrocarbon radicals having 1 to 14 carbon atoms and are alike or different; f is 0 to 1.5; g is 0 or 1; and e + f + g = 3. Examples of suitable R, R', R'', and R'' radicals are: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, 2-methylpentyl, heptyl, octyl, isooctyl, 2-ethylhexyl, 5,5-dimethylhexyl, nonyl, isodecyl, undecyl, dodecyl, cyclohexyl, cycloheptyl, and cyclooctyl. Examples of suitable R and R' radicals are phenyl, phenethyl, methoxyphenyl, benzyl, tolyl, xylol, naphthal, and methyl-naphthyl. Some examples of useful cocatalyst are triisobutylaluminum, trihexylaluminum, di-isobutylaluminum, hydride, dihexylaluminum hydride, di-isobutylhexylaluminum, trimethylaluminum, triethylaluminum, diethylaluminum chloride, $Al_2(C_2H_5)_3Cl_3$, and $Al(C_2H_5)_2(OC_2H_5)$.

Silica is the preferred support for the catalyst precursor. Other suitable inorganic oxide supports are aluminum phosphate, alumina, silica/alumina mixtures, silica pretreated with an organoaluminum compound such as triethylaluminum, and silica modified with diethylzinc, such modifier being used in a quantity

sufficient to react with the hydroxyl groups on the support which otherwise tend to react with and deactivate part of the titanium in the catalyst, but not in sufficient quantity to function as a cocatalyst. A typical support is a solid, particulate material essentially inert to the polymerization. It is used as a dry powder having an average particle size of about 10 to 250 microns and preferably about 30 to about 100 microns; a surface area of at least about 3 square meters per gram and preferably at least about 50 square meters per gram; and a pore size of at least about 80 Angstroms and preferably at least about 100 Angstroms. Generally, the amount of support used is that which will provide about 0.01 to about 0.5, and preferably about 0.2 to about 0.35 millimole of transition metal per gram of support. Impregnation of the abovementioned catalyst precursor into, for example, silica is accomplished by mixing the complex and silica gel in the electron donor solvent followed by solvent removal under reduced pressure and/or elevated temperature.

In preparing the polymer by the gas phase tandem reactor process, it is preferred that the titanium/magnesium precursor not be combined with the hydrocarbyl aluminum cocatalyst prior to being fed to the first reactor, but that these components be fed to such reactor separately, and that an additional quantity of the hydrocarbyl aluminum cocatalyst be fed to the second reactor in an amount sufficient to increase catalyst activity in the second reactor. However, in such a tandem reactor process, it is not necessary to prereduce or activate the titanium/magnesium complex with an amount of cocatalyst prior to feeding the complex to the first reactor. The cocatalyst is fed to each reactor neat or as a solution in an inert solvent such as isopentane.

In preparing the HMW and LMW components separately in gas phase reactors, the titanium/magnesium complex may be partially activated with cocatalyst prior to being fed to the reactor. In this case the cocatalyst used for the partial activation may be the same or different from that fed separately to each reactor. Preferred cocatalysts for partial activation of the titanium/magnesium complex prior to its being fed to the reactor are tri-n-hexylaluminum, diethylaluminum chloride, triethylaluminum and triisobutylaluminum, or a mixture of any of these.

Broad, exemplary ranges and preferred ranges of molar ratios of various components of the foregoing catalyst systems utilizing titanium/magnesium complexes are as follows:

Table I

Catalyst Components	Broad Exemplary Range	Preferred Range
1. Mg:Ti	0.5:1 to 56:1	1.5:1 to 5:1
2. Mg:X	0.005:1 to 28:1	0.075:1 to 1:1
3. Ti:X	0.01:1 to 0.5:1	0.05:1 to 0.2:1
4. Mg:ED	0.005:1 to 28:1	0.15:1 to 1.25:1
5. Ti:ED	0.01:1 to 0.5:1	0.1:1 to 0.25:1
6. Cocatalyst used as Partial Activator:		
Ti	0:1 to 50:1	0:1 to 5:1
7. Total Cocatalyst:		
Ti	0.6:1 to 250:1	11:1 to 105:1
8. ED:Al	0.05:1 to 25:1	0.2:1 to 5:1

Specific examples of the desired catalysts comprising a titanium/magnesium complex, and methods for their preparation are disclosed, for example, in U.S. Patent Nos. 3,989,881; 4,124,532; 4,174,429; 4,349,648; 4,379,759; 4,719,193; and 4,888,318; and European Patent application Publication Nos. 0 012 148; 0 091 135; 0 120 503; and 0 369 436; and the entire disclosures of these patents and publications pertaining to catalysts are incorporated herein by reference.

Another class of catalysts which may be used in the process of this invention is prepared by treating a previously dried, solid, inorganic, porous carrier containing OH groups, e.g., silica, with a liquid, e.g., tetrahydrofuran, containing a hydrocarbyl magnesium, e.g. ethylmagnesium chloride, evaporating liquid from the so-treated carrier leaving a magnesium precipitate on the carrier surface, and contacting the resulting

powder with a solution of transition metal compound e.g., a tetravalent titanium compound such as titanium tetrachloride, to form a transition metal/Mg complex or mixture of complexes on the surface of the carrier. The carrier may be initially dried in the presence of an oxygen-containing gas such as air rather than an inert gas such as nitrogen. The resulting supported transition metal/Mg complex may be utilized with a hydrocarbyl aluminum cocatalyst as disclosed previously with other Ti/Mg complexes, added to the first or both reactors. If hydrocarbyl aluminum cocatalysts are added to both reactors, they may be the same or different. Various catalysts of this type and methods of preparing the are described in U.S. Patent Nos. 4,481,301 and 4,562,169, the entire disclosures of which are incorporated herein by reference.

The amount of cocatalyst utilized in the Ziegler-Natta catalyst employed in the process of making the products of this invention whether for pre-reduction or activation of the catalyst prior to polymerization or added to the sole reactor or the first reactor of a tandem reactor process or both, is generally in the range, for example, of about 2 to 100 gram atoms of cocatalyst metal, e.g., aluminum, per gram atom of transition metal, e.g., titanium, preferably about 5 to 50 gram atoms of cocatalyst metal per gram atom of transition metal. Any amount of cocatalyst added to the second reactor is not included in the foregoing ranges. However, it is preferred that additional cocatalyst be fed to the second reactor to increase catalyst activity.

Referring now to the drawing, catalyst component containing transition metal e.g. titanium, is fed into first reactor 1 through line 2. Ethylene, comonomer, e.g., 1-hexene, if used, hydrogen, if used, inert gas such as nitrogen, if used, and cocatalyst, e.g. triethylaluminum (TEAL), are fed through line 3 into recycle line 4 where they are combined with recycle gas and fed into the bottom of reactor 1. The gas velocity is high enough and the size and density of the particles in reactor 1 are such as to form a fluidized or dense bed 5 comprising catalyst particles associated with polymer formed by the polymerization of ethylene and, if present, comonomer within reactor 1. The conditions in reactor 1, e.g. partial pressure of ethylene, hydrogen/ethylene molar ratio, temperature, total pressure, etc. are controlled such that the polymer which forms is of relatively high molecular weight (HMW). Recycle gas leaving the top of reactor 1 through line 4 is recompressed in compressor 6, cooled in heat exchanger 7 after passing through valve 8 and are fed to the bottom of reactor 1 after being optionally combined with make-up gases and cocatalyst from line 3 as described.

Periodically, when sufficient HMW polymer has formed in reactor 1, the polymer and catalyst are transferred to discharge tank 9 by opening valve 10 while valves 11, 12 and 13 remain closed. When an amount of the HMW polymer and catalyst from reactor 1 which is desired to be transferred has been fed to discharge tank 9, the transfer system to second reactor 14 is activated by opening valve 13 to force the HMW polymer and catalyst into transfer hose 15. Valve 13 is then closed to isolate transfer hose 15 from discharge tank 9 and valve 11 is opened, ensuring that any gases leaking through valve 13 are vented and do not back-leak across valve 10 into reactor 1. Transfer hose 15 is then pressurized with reactor-cycle gas from reactor 14 by opening valve 16. To minimize upsets in reactor 14, surge vessel 17 is used to store gas for pressuring transfer hose 15. With valve 16 still in the open position, valve 18 is opened to convey HMW polymer and catalyst into reactor 14. Both valves 16 and 18 are left open for a period to sweep transfer hose 15. Valves 18 and 16 are then closed sequentially. Transfer hose 15 is then vented by opening valve 13, valve 11 having remained open during the transfer operation. Discharge tank 9 is then purged with purified nitrogen through line 18A by opening valve 12.

During the transfer, cycle gas comprising hydrocarbons and hydrogen leaves reactor 14 through line 19, is compressed by compressor 20, flows through valves 21, 22 and 23 in line 24 and through surge tank 17, valve 16 and pressurized transfer hose 15 as described, thus effecting the transfer of HMW polymer and catalyst to reactor 14.

After the transfer to reactor 14 is effected, the flow of gas from reactor 14 to transfer hose 15 is stopped by closing valves 21, 22, 23 and 16. Ethylene, hydrogen, comonomer, e.g., 1-hexene, if used, inert gas such as nitrogen, if used, and cocatalyst or catalyst component, e.g., TEAL, are fed to reactor 14 through line 25 after being combined with unreacted cycle gas leaving the top of reactor 14 through line 19 which is compressed in compressor 20, cooled in heat exchanger 26 and enters the bottom of reactor 14 through line 27. The gas velocity and size and density of the particles in reactor 14 are such as to form fluidized or dense bed 28 of bimodal polymer particles associated with the catalyst, including the transition metal primary catalyst component added to reactor 1. The conditions in reactor 14, e.g., partial pressure of ethylene, hydrogen/ethylene ratio and temperature, are controlled such that a relatively low molecular weight (LMW) polymer forms primarily on and within the HMW polymer/catalyst particles transferred from reactor 1. After a sufficient amount of LMW polymer has formed resulting in a bimodal polymer having a desirable molecular weight distribution and other properties, the polymer is transferred to discharge tank 29 by opening valve 30 while keeping valve 31 closed. After substantially all the polymer has been transferred to discharge tank 29, it is collected by closing valve 30 and opening valve 31, resulting in the pressure

discharge of the final polymer product through line 32.

The following Examples illustrate the invention. The elasticity and viscosity values were all determined at 0.1 rad/sec.

5 Example 1

A catalyst was prepared by reacting $MgCl_2$, tetrahydrofuran (THF) and $TiCl_3 \cdot 0.33 AlCl_3$, adding the resulting complex to dehydrated silica treated with sufficient triethylaluminum to react with the OH groups in the silica but not enough to function significantly as partial activator or cocatalyst, and drying the resulting silica supported catalyst precursor. The procedure used to prepare the catalyst was substantially that of Example 4 of U.S. Patent No. 4,888,318 except that the partial activation of the supported magnesium and titanium precursor with tri-n-hexylaluminum and diethylaluminum chloride, as shown in the patent, was omitted. The free flowing catalyst powder contained the following weight percentages of components: Ti, 1.13; Mg, 1.95; Cl, 8.22; THF 15.4; and Al, 1.41.

Using the foregoing catalyst, a gas phase, fluidized bed polymerization process was carried out using two reactors operating in the tandem mode as shown in the drawing. The process included the feeding of 1-hexene as comonomer and triethylaluminum (TEAL) as cocatalyst to both reactors. Nitrogen was used to control the total pressure in both reactors at about 300 psig. Averages of other conditions in both reactors, which were controlled to produce a HMW-HDPE bimodal resin suitable for being blown extruded into low gauge films with superior mechanical properties, are shown in Table I, wherein " PC_2 =" is the partial pressure of the ethylene, " H_2/C_2 " is the molar ratio of hydrogen to ethylene, and " C_6/C_2 " is the molar ratio of 1-hexene to ethylene in the gas phase.

Table I

	Reactor 1 (HMW)	Reactor 14 (LMW)
Temp. ($^{\circ}C$)	75	105
PC_2 = (psi)	55-65	84-90
H_2/C_2	0.03	2.0
C_6/C_2	0.035-0.045	0.03
TEAL (ppmw)	290	190
Resid. Time (hrs)	2.8	3.6

The HMW polymer leaving reactor 1 was found by direct measurement to have a flow index (I_{21}) of 0.35 g/10 min., a flow ratio (FR) of 11, a dynamic elasticity of 0.56 at a complex viscosity of $4.1E6$ (4.1×10^6) poises, and a density of 0.931 g/cc, while the LMW polymer produced in reactor 14 was calculated from a single reactor process model to have a melt index (I_2) of about 400 g/10 min. and a density of 0.966 g/cc.

The granular bimodal polymer obtained from reactor 14 had a fraction of HMW component of 0.57. In this example and in Examples 2, and 4 to 7, the final polymer contained about 4 to 7 ppm of titanium ash. This is an indication of the amount of titanium precursor used in the process since substantially all the titanium in such precursor is present in the final polymer.

Using standard procedures and a Banbury mixer and Sterling extruder, the granular bimodal polymer from reactor 14 was compounded into pellets having a flow index (I_{21}) of 6.1 g/10 min., a MFR of 116, a density of 0.946 g/cc, and a dynamic elasticity of 0.598 at a corresponding complex viscosity of $1.1E6$ poises. The rheological properties, i.e., of elasticity and viscosity, of the HMW component and the bimodal polymer blend were measured in the Rheometric System IV at $200^{\circ}C$ under dynamic oscillatory mode in parallel plate geometry.

The bimodal polymer pellets were blown extruded into films on a 50 mm Alpine extruder equipped with a grooved barrel extruder, a 100 mm die and 1 mm die gap. The other extruder conditions were: melt temp = $416^{\circ}F$; frost line height = 36 inches; blow-up ratio = 4.0; nominal film gauge = 0.5 mil; output = 120 lbs./hr. The films were found to have a Dart Drop Impact (F_{50}) of 400 g and a MD Tear of 26 g/mil. Contrary to what is expected in the art, these properties were achieved despite the fact that the bimodal polymer was found to have a higher degree of short chain branching in the LMW component than in the HMW component.

Example 2

The procedure of Example 1 was followed using slightly different process conditions as shown in Table II:

Table II

	Reactor 1 (HMW)	Reactor 14 (LMW)
Temp. (°C)	75	105
PC ₂ = (psi)	68	86
H ₂ /C ₂	0.03	1.7
C ₆ /C ₂	0.04	0.04
TEAL (ppmw)	300	300
Resid. Time (hrs)	3.0	4.0

The HMW component leaving reactor 1 was found by direct measurement to have the following properties: l_{21} = 0.45 g/10 min.; FR = 10; dynamic elasticity = 0.59 at a complex viscosity of 4.0E6; and density = 0.931 g/cc; the LMW was calculated to have a melt index (l_2) of 450 (estimated from GPC) and a density of 0.964 g/cc; and the pellets prepared from the granular bimodal blend polymer from reactor 14 had the following properties: HMW weight fraction = 0.57; l_{21} = 6.7 g/10 min.; MFR = 106; dynamic elasticity = 0.60 at a complex viscosity of 9.3E5 poises; and density = 0.945 g/cc. Films prepared from the bimodal polymer blend as described in Example 1 had a Dart Drop Impact (F_{50}) of 406 g and an MD Tear of 28 g/mil.

Example 3

A catalyst was prepared as follows: In part A of the preparation, 289.5 grams of Davison 955-800 silica having a nominal average particle size of 50 microns were transferred into a 4-neck 3-liter round bottom flask fitted with an overhead stirrer and under a slow purge of nitrogen. About 1500 ml of dry tetrahydrofuran (THF) were added to the flask which was placed into an oil bath set at 60-65 °C.

Next 184 ml of a 2.0 molar solution of ethylmagnesium chloride in THF was added dropwise using an addition funnel to the silica/THF slurry. After 10 minutes, the THF was removed by distillation to yield a white free flowing powder. The powder was dried for 16 hours under a slow nitrogen purge with the oil bath set at 80-85 °C, and, except for 2 grams which were removed from the flask, constitute the part A product. The powder was found to contain 6.0 wt.% of THF.

In part B of the preparation, 1500 mls of heptane as received was placed into a 3-liter round bottom flask, and 162 ml of neat titanium tetrachloride was added dropwise to the heptane using an addition funnel. This solution was then siphoned into the part A product. The slurry was stirred for 1.5 hours with the oil bath at 80-85 °C after which the silica was allowed to settle and the reaction solution was decanted through a gas dispersion tube under a slight nitrogen pressure. The silica was then washed six times with about 1500 mls of dry hexane. After the last wash, the silica was dried with a nitrogen purge to yield 370 grams of a very light tan catalyst precursor. Analysis: Mg = 2.52 wt.%, Ti = 3.36 wt.%, THF = 3.2 wt.%.

The foregoing catalyst was used to carry out a two stage, HMW first, gas phase fluidized bed process in the tandem mode as illustrated in the drawing and similar to that described in Example 1, under conditions such as to produce a high molecular weight, high density ethylene polymer film resin in accordance with this invention. As cocatalyst, triethylaluminum (TEAL) was fed to the first (HMW) reactor and trimethylaluminum (TMA) to the second (LMW) reactor. Ranges of reaction conditions employed are shown in Table III.

Table III

	Reactor 1 (HMW)	Reactor 14 (LMW)
Temp. (° C)	75	98
PC ₂ = (psi)	30	60
H ₂ /C ₂	0.03	2.4
C ₆ /C ₂	0.04	0.042
TEAL (ppmw)	330	0
TMA (pppw)	0	660
Resid. Time (hrs)	5.0	4.0

The HMW polymer leaving reactor 1 was found by direct measurement to have the following properties: l_{21} = 0.30 g/10 min.; FR = 15; dynamic elasticity = 0.66 at a complex viscosity of 4.2E6; and density = 0.930 g/cc; the LMW component was calculated to have a melt index (l_2) of 550 (estimated from GPC) and an estimated density of 0.965 g/cc; and pellets prepared from the granular bimodal polymer from reactor 14 had the following properties: HMW weight fraction = 0.57; l_{21} = 8.8 g/10 min.; MFR = 140; dynamic elasticity = 0.587 at a complex viscosity of 9.5E5 poises; and density = 0.945 g/cc. In addition, the polymer had a titanium ash content of about 12 to 18 ppm. Films prepared from the bimodal polymer blend as described in Example 1 had a Dart Drop Impact (F_{50}) of 387 g and a MD Tear of 22 g/mil.

Example 4

HMW and LMW components intended to be physically blended in producing an HMW-HDPE bimodal polymer in accordance with this invention were separately prepared in a single stage gas phase reactor. The catalyst used to prepare the HMW component was the same as that described in Example 1. The catalyst used to prepare the LMW component was the catalyst of Example 1 subjected to prereduction or partial activation with tri-n-hexylaluminum, as cocatalyst. The procedure used to prepare the catalyst was substantially that of Example 4 of U.S. patent No. 4,888,318 except that the partial activation of the supported magnesium and titanium precursor was carried out with tri-n-hexylaluminum alone as partial activator rather than the latter together with diethylaluminum chloride as shown in the patent. The free flowing catalyst powder contained the following weight percentages of components: Ti, 1.07; Mg, 1.7; Cl, 7.5; THF, 14.3; and Al, 1.98.

Reactor conditions employed in the preparation of the two components are shown in Table IV.

Table IV

	HMW	LMW
Temp. (° C)	80	98
PC ₂ = (psi)	84	78
H ₂ /C ₂	0.02	1.72
C ₆ /C ₂	0.008	0.085
TEAL (ppmw)	400	400
Resid. Time (hrs)	2.0	2.0

The HMW component had the following properties: l_{21} = 0.3 g/10 min.; FR = 10; dynamic elasticity = 0.64 at a complex viscosity of 5.0E6 poises; and density = 0.935 g/cc; while the LMW component had a melt index (l_2) of 300 g/10 min. and a density of 0.950 g/cc.

A blend of the HMW and LMW components was prepared by melt mixing in a Banbury mixer with a conventional stabilizer package to prevent degradation. The blend had the following properties: HMW weight fraction = 0.55; l_{21} = 5.8 g/10 min.; MFR = 90; density = 0.942 g/cc; and dynamic elasticity = 0.577 at a complex viscosity of 11.4E5 poises. A film prepared from the blend as described in Example 1 had a Dart Drop Impact (F_{50}) of 330 g and a MD Tear of 21 g/mil.

Example 5

The procedure of Example 4 was followed except that the blend contained a weight fraction of 0.50 of the HMW fraction prepared in a 3/4 inch Brabender twin screw extruder. The blend of HMW and LMW components had the following properties: I_{21} = 7.7 g/10 min.; MFR = 101; density = 0.9624 g/cc; and dynamic elasticity = 0.516 at a complex viscosity of 9.3E5 poises. The bimodal polymer blend could be formed into low gauge films as described in Example 1 having excellent mechanical properties, e.g., Dart Drop Impact and MD Tear.

10 Example 6

The procedure of Example 5 was generally followed except that the catalyst of Example 1, which was not partially activated, was used to prepare both the HMW and LMW polymers, and the conditions in the HMW and LMW reactors were as shown in Table V.

15 Table V

	HMW	LMW
Temp. (°C)	74	105
PC ₂ = (psi)	24	87
H ₂ /C ₂	0.018	1.44
C ₆ /C ₂	0.098	0.0002
TEAL (ppmw)	320	400
Resid. Time (hrs)	2.8	2.4

The HMW component had the following properties: I_{21} = 0.38 g/10 min.; FR = 11; dynamic elasticity = 0.615 at a complex viscosity of 4.16E6 poises; and density = 0.926 g/cc; while the LMW component had a melt index (I_2) of 250 g/10 min. and a density of 0.960 g/cc.

A blend of the HMW and LMW components prepared as described in Example 4 had the following properties: HMW weight fraction = 0.52; I_{21} = 9.9 g/10 min.; MFR = 115; density = 0.942 g/cc; and dynamic elasticity = 0.517 g/10 min. at a complex viscosity of 8.0E5 poises. A 1 mil film prepared from the blend as described in Example 1 had a Dart Drop Impact (F_{50}) of 387 g, a MD Tear of 26 g/mil., and a TD Tear (Elmendorf tear resistance in the transverse direction) of 57 g/mil.

35 Example 7

The procedure of Example 6 was followed using the same HMW and LMW components except that such components were blended in a different proportion. The blend had the following properties: HMW weight fraction = 0.58; I_{21} = 5.7 g/10 min.; MFR = 94; density = 0.940 g/cc; and dynamic elasticity = 0.522 at a complex viscosity of 10.2E5 poises. A 1 mil film prepared from the blend as described in Example 1 had a Dart Drop Impact (F_{50}) of 305 g, a MD Tear of 23 g/mil. and a TD Tear of 375 g/mil.

The results of the foregoing examples indicate that HMW-HDPE resins of this invention can be blown extruded into low gauge films having superior mechanical properties.

Before being formulated into films, the polymers of this invention may be compounded with various additives utilized in relatively minor amounts, e.g., other polymers such as conventional low-density polyethylene (LDPE) and recycled polyethylene, stabilizers, anti-oxidants, plasticizers, fillers, etc., as are well known in the art.

50 Claims

1. An ethylene polymer comprising a preponderance of polymerized ethylene having a density of at least 0.925 g/cc, a flow index or high load melt index (I_{21}) no higher than 15 g/10 min., a melt flow ratio (MFR) of at least 65, and a dynamic elasticity at 0.1 rad./sec. of no higher than 0.7 at a corresponding complex viscosity at 0.1 rad./sec. no higher than about 14E5 (14×10^5) poises.
2. A polymer according to claim 1 which consists essentially of either 1) a homopolymer of ethylene; 2) at least one copolymer of a preponderance of ethylene with a minor amount of a 1-olefin containing 3 to

10 carbon atoms as comonomer; or 3) a mixture thereof.

3. A polymer according to claim 1 or 2 where in the amount of polymerized comonomer is from 0 to 20 weight percent, based on the total weight of polymer.

4. A polymer according to any preceding claim wherein the comonomer comprises 1-hexene.

5. A polymer according to any preceding claim having a density from 0.940 to 0.960 g/cc, an I_{21} from 4 to 12 g/10 min., a MFR from 75 to 180, and a dynamic elasticity from 0.45 to 0.65 at a corresponding complex viscosity from 6E5 to 14E5 poises.

6. A polymer according to claim 5 having a density from 0.943 to 0.952 g/cc, an I_{21} from 5 to 10 g/10 min., a MFR from 80 to 150, and a dynamic elasticity from 0.45 to 0.60 at a corresponding complex viscosity from 7E5 to 14E5 poises.

7. A polymer according to any preceding claim consisting essentially of a blend of at least 0.5 weight fraction of a relatively high molecular weight (HMW) component having a density of at least 0.910 g/cc, a flow index or high load melt index (I_{21}) of no higher than 0.8 g/10 min., a relatively narrow molecular weight distribution indicated by a flow ratio (FR) no higher than 15, and a dynamic elasticity at 0.1 rad/sec., of no higher than 0.75 at a corresponding complex viscosity at 0.1 rad/sec. of no higher than 7E6, with a relatively low molecular weight (LMW) component having a density of at least 0.940 g/cc and a melt index (I_2) of at least 100 g/10 min.

8. A polymer according to claim 7 wherein the HMW component is present at a weight fraction of 0.5 to 0.65, and has a density of 0.920 to 0.935 g/cc, an I_{21} of 0.15 to 0.7 g/10 min., a FR of 8 to 14, and a dynamic elasticity of 0.45 to 0.7 at a corresponding complex viscosity of 2E6 to 6E6 poises, and the LMW component has a density of 0.945 to 0.970 g/cc and an I_2 of 200 to 2000 g/10 min.

9. A polymer according to claim 8 wherein the HMW component is present at a weight fraction of 0.51 to 0.60, and has a density of 0.924 to 0.935 g/cc, an I_{21} of 0.2 to 0.6 g/10 min., a FR of 9 to 13, and a dynamic elasticity of 0.5 to 0.65 at a corresponding complex viscosity of 3E6 to 6E6 poises, and said LMW component has a density of 0.950 to 0.970 g/cc and an I_2 of 300 to 1500 g/10 min.

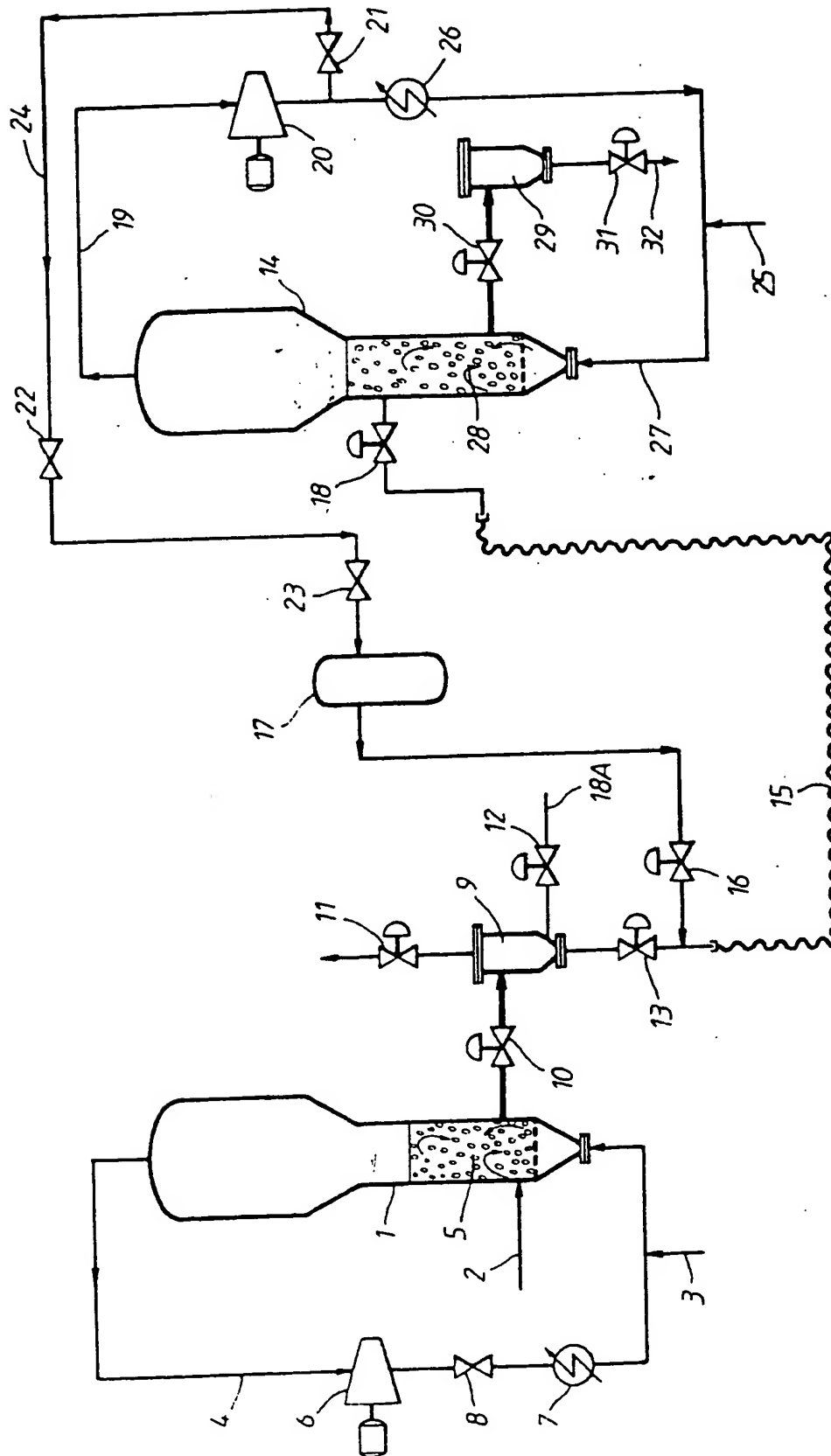
10. A film comprising a polymer according to any preceding claim, the film having a thickness up to 1.5 mil and a Dart Drop Impact (F_{50}) of at least 200 g and a MD Tear of at least 10 g/mil.

11. A film according to claim 10 having a Dart Drop Impact (F_{50}) of 200 to 600 g and a MD Tear of 15 to 60 g/mil.

12. A film according to claim 11 having a Dart Drop Impact (F_{50}) of 200 to 600 g and a MD Tear of 20 to 60 g/mil.

13. A polymer blend according to any of claims 7 to 9 produced by a process comprising contacting in a first gas phase, fluidized bed reaction zone under polymerization conditions, a gaseous monomeric composition comprising a major proportion of ethylene and, optionally, hydrogen, with a Ziegler-Natta or coordination catalyst comprising a transition metal compound as hereinafter defined as primary catalyst component and a hydrocarbyl aluminum as reducing cocatalyst, the hydrogen/ethylene molar ratio (H_2/C_2 ratio) being no higher than 0.3 and the ethylene partial pressure being no higher than 100 psia, to produce the HMW component associated with catalyst particles, transferring the HMW/catalyst particles to a second gas phase, fluidized bed reaction zone into which is also fed hydrogen and a gaseous monomeric composition comprising a major proportion of ethylene, under polymerization conditions including a H_2/C_2 ratio of at least 0.9 and at least 8.0 times that in the first reaction zone, and an ethylene partial pressure of at least 1.2 times that in the said first reaction zone, to produce the LMW component deposited on and within the HMW polymer/catalyst particles, the transition metal compound being either 1) a complex supported on an inorganic porous carrier and having the empirical formula $Mg_aTi(OR)_bX_c(ED)_d$ wherein R is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR group is alike or different; X is Cl, Br, or I, or mixtures thereof; ED is an electron donor,

which is a liquid Lewis base in which the precursors of the titanium based complex are soluble; a is 0.5 to 56; b is 0, 1, or 2; C is 1 to 116; and d is 2 to 85, the complex being formed by r acting a compound having the formula $Ti(OR)_aX_b$ wherein R and X are as defined for the formula of the complex, a is 0, 1 or 2; b is 1 to 4; and a+b is 3 or 4, with a compound having the formula M_gX_2 wherein X is as defined for the formula of the complex, in the presence of the electron donor ED; or 2) a complex prepared by treating a previously dried, solid, inorganic, porous carrier containing OH groups, with a liquid containing a hydrocarbyl magnesium, evaporating liquid from the so-treated carrier leaving a magnesium precipitate on the carrier surface, and contacting the resulting powder with a solution of a tetravalent titanium compound to form a Ti/Mg complex or mixture of complexes on the surface of the carrier.





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 6000

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 369 436 (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY INC.) * claim 1 *	1-13	C08F297/08 C08F10/02 C08F2/34 C08F4/655
X	--- PATENT ABSTRACTS OF JAPAN vol. 9, no. 32 (C-265)(1755) 9 February 1985 & JP-A-59 179 507 (TOA NENRYO KOGYO KABUSHIKI KAISHA) * abstract *	1-13	
X	--- PATENT ABSTRACTS OF JAPAN vol. 9, no. 32 (C-265)(1755) 9 February 1985 & JP-A-59 179 508 (TOA NENRYO KOGYO KABUSHIKI KAISHA) * abstract *	1-13	
E	--- EP-A-0 503 791 (MOBIL OIL CORPORATION) * claim 1 *	1-13	
A	--- EP-A-0 231 102 (MOBIL OIL CORPORATION) * claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
D	& US-A-4 888 318		C08F
A	--- EP-A-0 192 427 (BP CHEMICALS LTD.) * claim 1 *	13	

The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 NOVEMBER 1992	Examiner SERRAVALLE M.
CATEG RY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons @ : member of the same patent family, corresponding document	